

## STUDIES OF THE FORMATION, STRUCTURE, AND REACTIVITY OF NANOPARTICULATE GOETHITE

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### RESEARCH OBJECTIVES

Goethite is a ubiquitous mineral in soils and sediments, and recent work (Van Der Zee et al., 2003) suggests that on the nanoscale it is also the dominant Fe oxyhydroxide in lacustrine and marine sediments. Goethite nanoparticles may have markedly different properties than their larger analogs, including sorption capabilities, surface charges, aggregation, and redox capability (Waychunas et al., 2005). In analogy to our work with nanosize sphalerite (Gilbert et al., 2004), there may also be important phase transformations in both molecular and magnetic structure as a function of size. We thus wish to prepare monodispersed nanogoethite from a few nanometers to 100 nm in diameter, and determine the changes in structure and chemical reactivity over this range.

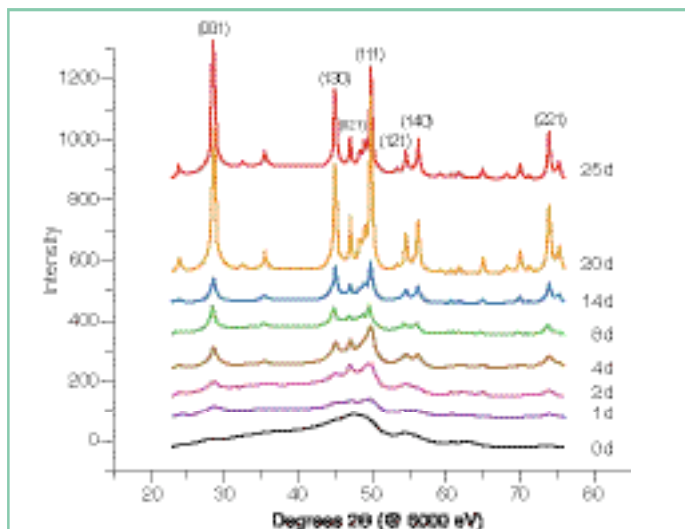


Figure 1. Synchrotron x-ray diffraction patterns of nanogoethite grown for varying periods at 90°C obtained on ALS beamline 7.3.3. Goethite Bragg peaks are labeled with Miller indices. Particle size ranges from 4 nm (0 days) to ~100 nm (25 days).

### APPROACH

Nanogoethites were prepared by rapid microwave heating of a ferric nitrate solution, followed by rapid cooling. The resultant solution was aged for up to 33 days at 90°C, with aliquots taken during this period having progressively larger crystallites. Size distributions were obtained via dynamic light scattering (DLS), small angle x-ray scattering (SAXS), and via transmission electron microscopy (TEM) measurements. The crystallization process was also studied in real time by SAXS studies at the Advanced Photon Source (APS). Crystallites were monodispersed and from 4 to 120 nm in diameter, with shape variations during growth. The smallest crystallites were equiaxial, but assembled into rodlike forms in the 30 nm size range. Wide-angle x-ray scattering patterns were obtained for all goethites, including a

series over the full coarsening period (Figure 1), and a more detailed analysis of the smallest crystallites at the APS. Sorption of a series of metals (Hg, Zn, As [as arsenate], and Cu) was done over the whole size range, and the samples studied via extended x-ray absorption fine structure (EXAFS) analysis at SSRL.

### ACCOMPLISHMENTS

All the sorption studies indicated a change in the character of the metal sorption complexes in the smallest nanogoethites, suggesting differences in the nature of the surface attachment sites. X-ray scattering studies were also consistent, with the smallest crystallites deviating in structure from bulk goethite. Ongoing work involves examining how the nanogoethites change with aging at low temperatures, and the precise nature of aggregation. TEM analysis suggests oriented aggregation processes occur at the smaller size regimes (4–10 nm), leading to nonclassical growth, while larger (30+ nm) nanogoethite grows by classical monomer addition.

### SIGNIFICANCE OF FINDINGS

The results verify that nanogoethite reacts differently from larger sized crystallites and has different molecular surface structure. This suggests that studies done with coarser samples may overlook processes that would occur in sediments where goethite is forming. There also may be changes in sorbed species as nanogoethite ages, particularly when oriented aggregation occurs.

### RELATED PUBLICATIONS

- Gilbert, B., H. Zhang, F. Huang, J. Banfield, Y. Ren, D. Haskell, J. Lang, G. Srajer, A. Jurgensen, and G. Waychunas, Analysis and simulation of the structure of nanoparticles that undergo a surface-driven structural transformation. *J Chem Phys*, 120, 11785–11795, 2004.
- van der Zee, C., D.R. Roberts, D.G. Rancourt, and C.P. Slomp, Nanogoethite is the dominant reactive oxyhydroxide phase in lake and marine sediments. *Geology*, 31, 993–996, 2003.
- Waychunas, G.A., C.S. Kim, and J.F. Banfield, Nanoparticulate iron oxide minerals in soils and sediments: Unique properties and contaminant scavenging mechanisms. *J. Nanoparticulate Research* (in press), 2005.

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